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(54) Catalytic cracking process.

(57) Catalytic cracking processes wherein the cracking catalysts are prepared by: (1) contacting a mixture of a large pore zeolite and an inorganic oxide matrix at effective conditions of temperature, pH and time with a fluoro salt; and (2) ammonium exchanging the product of step (1) to provide a catalyst having less than 0.3 percent by weight Na_2O , based on total catalyst weight, or less than 2.0 percent by weight of the zeolite employed in the catalyst. Optionally, the zeolite used is provided with an effective amount of at least one cation selected from the class consisting of cerium, lanthanum, praseodymium, neodymium, promethium, samarium, europium, lutetium, gadolinium, terbium, dysprosium, holmium, erbium, thulium and ytterbium.

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CATALYTIC CRACKING PROCESS

CROSS-REFERENCE TO RELATED APPLICATIONS

5 This application is a continuation of prior U.S. Application Serial No. 848,034, filed April 4, 1986, which is a division of Serial No. 657,413, filed October 4, 1984 (now U.S. Patent No. 4,588,701), and of Serial No. 848,033, filed April 3, 1986, which is a division of Serial No. 659,641 filed October 4, 1984, now U.S. Patent No. 4,591,576.

FIELD OF THE INVENTION

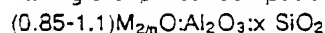
10 The present invention relates to new catalytic cracking catalysts, their method of manufacture and to cracking processes employing such catalysts. The cracking catalysts comprise an inorganic oxide matrix and a large pore zeolite (6Å to 15Å) and are formed by a process that achieves a low concentration of sodium ions in the final catalyst without the requirement of energy intensive calcination steps heretofore employed for Na₂O removal.

BACKGROUND OF THE INVENTION

20 The prior art dealing with catalytic cracking catalysts is voluminous, with a basic underlying goal being the preparation of modified zeolites for use as cracking catalysts. These zeolites are then added to alumina, silica, etc., as a matrix for the zeolite. The zeolitic component has generally been zeolite Y and has essentially been unchanged for over a decade. The development of the art of cracking catalysts has centered, for the most part, on preparing catalyst formulations by employing pretreated zeolites which are then subsequently admixed with various matrices. Representative of such developments are those disclosed in U.S. Patent Nos. 3,140,249, 3,352,796, 3,312,615 and 3,542,670.

30 Another approach has been related to various secondary treatments for zeolites, such as processes to lower the alkali metal content of the basic zeolitic component (e.g., U.S. Patent No. 3,293,192 and Re. 28,629) and processes to extract aluminum from the zeolitic framework (to enhance the thermal stability of the zeolite). Of course, the latter processes necessarily result in products having sites where aluminum has been removed, and accordingly, the zeolites formed by such a process have a certain instability as a result.

35 In EPC Application 81110620.3, having EPC Publication No. 82,211 and published June 29, 1983, and in U.S. Patent No. 4,503,023 incorporated herein by reference thereto, a new class of zeolites is disclosed and denominated therein as zeolite "LZ-210". This class of aluminosilicates comprises aluminosilicates having a chemical composition expressed in terms of mole ratios of oxides as:



40 wherein "M" is a cation having the valence "n", and "x" has a value greater than 6.0. LZ-210 is a new class of aluminosilicates having a faujasite structure and having an SiO₂ to Al₂O₃ ratio greater than 6.0 while not having the problems necessarily associated with dealuminated, i.e., aluminum extracted, zeolites.

45 Among the various prior art processes are processes involving the treatment of zeolites with halogen-containing compounds whereby residual fluoride is provided to the zeolite. Representative of patents for such processes are U.S. Patent Nos. 3,620,960 (molybdenum fluoride); 3,630,965 (hydrofluoric acid); 3,644,220 (volatile halides selected from the group consisting of aluminum, zirconium, titanium, tin, molybdenum, tungsten, chromium, vanadium, antimony, bismuth, iron, platinum group metals and rare earths); 3,575,887 (fluorides and chlorides); 3,699,056 (halogenated hydrocarbons); 3,702,312 (fluorides and chlorides); 4,427,788 (ammoniacal aluminum fluoride solution for treatment of zeolites having a silica-to-alumina ratio greater than 100); and 4,427,790 (complex fluoroanion treatment of zeolites having a silica-to-alumina ratio greater than 100).

50 U.S. Patent No. 4,427,790 is a recent patent disclosing that certain fluoroanions provide enhancement in the activity of crystalline zeolite, but only when the zeolites have silica-to-alumina ratios greater than about 100. The patent also discloses the post-admixture of the treated products with matrix materials. Interestingly, the patent affirmatively teaches that the process is beneficial only for the treatment of such high silica

zeolites and only when such zeolites are treated in the absence of any other component. U.S. Patent No. 4,500,421 (a continuation-in-part of U.S. Patent No. 4,427,790) discloses processes for the treatment of high silica zeolites (i.e., with a silica/alumina ratio greater than 100) with reagents comprising fluoroanion moieties in solvent or solid media. The treated zeolites can be subjected to further treatments including hydrolysis, ammonium exchange and calcining, combined with an inorganic matrix or binder and used as catalysts in processes for the catalytic conversion of hydrocarbon feedstocks.

One variation of the above fluoride treatments for zeolites is disclosed in U.S. Patent No. 3,619,412. The process of U.S. Patent No. 3,619,412 comprises the treatment of a mixture of mordenite and amorphous silica-alumina with a solution of a fluorine compound such as ammonium difluoride or hydrofluoric acid. The hydrofluoric acid treatment is said to provide stability to the treated catalyst. Further, processes involving specific treatments of zeolites having silica-to-alumina ratios greater than 100 are disclosed in U.S. Patent Nos. 4,427,786; 4,427,787; 4,427,789 and 4,427,791. U.S. Patent No. 4,427,786 discloses the treatment of supported zeolites, wherein the zeolite has a silica-to-alumina ratio greater than 100, with boron fluoride, hydrolyzing of the of the boron fluoride, an ammonium salt exchange and calcination. A comparison of examples 2 and 9 therein shows that the activity of zeolites having a silica-to-alumina ratio of less than 70 showed a decrease in activity as a result of the process. U.S. Patent No. 4,427,787 discloses the treatment on an alumina-supported zeolite, said zeolite having a silica-to-alumina ratio greater than 100, with a dilute aqueous solution of hydrogen fluoride. The hydrogen fluoride treatment is said to preferentially increase the activity of zeolites having silica-to-alumina ratios over 100. U.S. Patent No. 4,427,789 discloses the treatment of an alumina-supported zeolite, said zeolite having a silica-to-alumina ratio greater than 100, with an aqueous solution of an alkali metal fluoride, impregnation with a warm solution of an ammonium salt and a calcination. U.S. Patent No. 4,427,791 discloses a process for the treatment of an inorganic oxide material with ammonium fluoride or boron trifluoride, ammonium exchange, and calcination. The treatment is said to enhance the activity of the inorganic oxide material as a result of the ammonium exchange step.

The use of LZ-210 and forms of LZ-210 as catalysts is disclosed in copending and commonly assigned U.S. Serial No. 490,965, filed May 2, 1983, now abandoned, and U.S. Serial No. 657,417, filed October 3, 1984 (now U.S. Patent No. 4,687,754), and U.S. Serial No. 500,446, filed June 2, 1983, now abandoned, and in U.S. Serial No. 721,894, filed April 11, 1985 (now U.S. Patent No. 4,711,864).

The instant invention relates to a new process wherein a large pore zeolite in combination with at least one inorganic oxide matrix component is contacted with solutions or slurries of specific fluoro salts of specific elements, as discussed hereinafter, to provide zeolite-containing catalyst useful in hydrocarbon conversion processes.

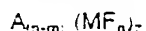
SUMMARY OF THE INVENTION

The above discussion of the prior art is instructive in appreciating the rather unusual and novel results observed in the instant invention. One of the most striking attributes of the instant invention is the heretofore unknown ability to achieve a catalyst comprising a large pore zeolite and inorganic oxide with a Na_2O content (weight percent) less than about 2.0 weight percent, based on the weight of the zeolite, or less than about 0.3 weight percent, based on the total catalyst weight, without the need of a calcination step to promote removal of Na_2O or by use of a commercially unrealistic number of ion exchange steps. Such a process has not heretofore been disclosed, wherein Y zeolites are employed as components in catalysts without the use of a calcination step during their preparation. In fact, the prior art discloses the contrary. For example, U.S. Patent No. 3,933,983 discloses treatment of a Y zeolite with solutions of ammonium fluorosilicate and ammonium sulfate. At column 12 of U.S. Patent No. 3,933,983 in Table IV, the treated samples all have a Na_2O content of greater than 3.35 percent by weight (dry basis). Table IV also discloses that it was necessary to calcine the zeolites at temperatures of 600° F prior to the rare earth exchange to achieve a reduction in the Na_2O content. Such calcination procedures have been employed heretofore in the prior art to provide for a thermal redistribution of the Na_2O present in the zeolite.

The instant process relates to the preparation of catalysts by treatment of a physical mixture of a large pore zeolite and an inorganic matrix with specific fluoro salts. The catalysts are useful in hydrocarbon conversion processes and in particular in catalytic cracking processes. Although the mechanism by which such novel catalysts are generated is not entirely understood, it is clear that the interactions of the zeolite, inorganic oxide matrix and the fluoro salt, in slurries having a pH greater than 3, or greater than 7 in an embodiment, are unique in their ability to provide a final catalyst having a Na_2O content less than about 2.0 percent, based on the zeolite weight, or 0.3 percent by weight based on the total catalyst weight, as characterized by the fact that such may be achieved without the requirement of a Na_2O calcination of the

catalyst or zeolite contained in the catalyst. Further, it is evident that separate treatment of the zeolite and inorganic oxide matrix with subsequent mixture to form the catalysts does not result in a catalyst having the same catalytic characteristics as the catalysts of the instant invention. Although a thermal calcination is not required to achieve catalysts having low Na_2O contents, it is clear that the treatment of mixtures of a large pore zeolite and an inorganic oxide matrix may provide beneficial results when such calcinations are carried out on the finished catalyst and accordingly, optional calcinations are not excluded from the scope of the instant invention.

The hydrocarbon conversion processes of the instant invention employ catalysts prepared by contacting a mixture of a large pore zeolite and an inorganic oxide matrix with an effective amount of a fluoro salt of the formula:



wherein "A" is an organic or inorganic ionic moiety, e.g., ammonium or quaternary ammonium ions; $A_{(n-m)}$ - $(MF_n)_z$ is a fluorocanion moiety comprising the element "M"; "M" is an element selected from the group of elements from Groups VB, VIB, VIIB, VIII, IIIA, IVA and VA of the Periodic Table of Elements (Sargent - Welch Scientific Company) and rare earth elements; representative of permissible elements, i.e., "M", are boron, aluminum, gallium, silicon, phosphorus, antimony, bismuth, palladium, platinum, iridium, iron, rhodium, molybdenum, tantalum and titanium; "n" is the coordination number of "M"; "m" is the valence of "M" and "z" is the valence or charge associated with "A". The fluoro salt is present in an effective amount and may be in the form of an aqueous solution or slurry. The effective amount of fluoro salt is preferably an amount of at least 0.0075 moles per 100 grams of the large pore zeolite on an anhydrous basis. The aqueous slurry of the fluoro salt, zeolite and inorganic oxide matrix component(s) has a pH greater than about 3, preferably having a pH within the range of about 3 to 7, more preferably between about 4 to 7, and most preferably between about 4 and about 6.5, and is employed at effective conditions of temperature and time. Alternatively, the aqueous solution or slurry of the fluoro salt, zeolite and matrix component has a pH greater than about 7, preferably having a pH within the range of 7.5 to about 9, more preferably between about 7.5 and about 8.5, at effective conditions of temperature and time. It has been found that catalysts processed at pH ranges of 3 to 7 generally have lower Na_2O contents, thus produce higher selectivity in catalytic cracking processes at the expense of some loss in activity. On the other hand catalysts processed at pH values greater than 7 have higher Na_2O contents than catalysts processed at pH 3 to 7 (but still lower than similar catalysts prepared without fluorocanion treatment), giving better crystallinity retention and higher catalyst activity in catalytic cracking, with somewhat lower selectivity.

The catalyst product obtained after the treatment with the fluoro salt is then preferably treated by ammonium exchange the product with ammonium ions, preferably in an amount of between about 1.0 to 10 moles of ammonium ions per 100 grams of the large pore zeolite, the weight of zeolite being on an anhydrous basis. The resulting catalysts have a Na_2O content less than about 2.0 percent by weight, preferably less than 1.5 and more preferably less than 1.0, based on the total weight of the large pore zeolite, or less than about 0.3 percent by weight, preferably less than 0.2 and more preferably less than 0.1, based on the total weight of the catalyst.

The above catalysts may be provided with a catalytically effective amount of at least one rare earth cation selected from the group consisting of cerium, lanthanum, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, lutetium, thulium and ytterbium to provide, preferably, between about 0.1 percent by weight and about 20 percent by weight, based on the total weight of the large pore zeolite employed in the catalyst, of at least one or more of the aforementioned rare earth cations.

The catalysts described herein have been patented, and accordingly the processes of the present invention for the catalytic conversion of hydrocarbons under effective conversion conditions, e.g., catalytic cracking of crude oil-derived feedstocks under effective cracking conditions, comprise contacting a feedstock as disclosed herein with at least one catalyst as claimed in U.S. Patent No. 4,588, 701 or 4,591,576, which patents are incorporated herein by reference thereto.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to processes for the use of new catalysts prepared by contacting a mixture of a large pore zeolite and an inorganic oxide matrix with an effective amount of a fluoro salt of the formula:



wherein "A" is an organic or inorganic ionic moiety, e.g., ammonium and quaternary ammonium ions; $A_{(n-m)}$ -

(MF_n)_z is a fluoroanion moiety comprising the element "M"; "M" is an element selected from the group of elements from Groups VB, VIB, VIIB, VIII, IIIA, IVA, and VA of the Periodic Table of Elements (Sargent - Weich Scientific Company) and rare earth elements, such as, for example, boron, aluminum, gallium, silicon, phosphorus, antimony, bismuth, palladium, platinum, iridium, iron, rhenium, molybdenum, tantalum and titanium; "n" is the coordination number of "M"; "m" is the valence of "M"; and "z" is the valence or charge associated with "A". The fluoro salt is employed in an effective amount to achieve the desired Na₂O level and is preferably an amount of at least 0.0075 moles per 100 grams of the large pore zeolite, on an anhydrous basis. The aqueous slurry of the fluoro salt, large pore zeolite and inorganic oxide matrix has a pH greater than 3, preferably having a pH within the range of about 4 to about 7, and more preferably between about 4 and about 6.5, and is reacted at effective conditions of temperature and time. Alternately, the aqueous solution or slurry of the fluoro salt, zeolite and matrix component has a pH greater than about 7, preferably having a pH within the range of 7.5 to about 9, more preferably between about 7.5 and about 8.5, and is reacted at effective conditions of temperature and time. The product is preferably treated by ammonium exchanging the resultant product of the fluoro salt treatment with ammonium ions, prefer in an amount of between about 1 mole to about 10 moles of ammonium ions per 100 grams of the large pore zeolite, on an anhydrous basis. The resulting catalysts have a Na₂O content less than about 2.0 percent by weight, preferably less than 1.5 and more preferably less than 1.0 percent by weight, based on the total weight of the large pore zeolite or less than about 0.3 percent by weight, preferably less than 0.2 and more preferably less than 0.1, based on the total weight of the catalyst, and such can be achieved without a Na₂O calcination, as described hereinafter. The Na₂O contents of the catalysts are described in alternative terms as based upon either the weight of the zeolite or the total weight of the catalyst since the finished catalyst is most easily analyzed for overall Na₂O content but the amount actually present in the zeolite component is believed to be at least partially responsible for the effectiveness of the catalyst. However, after treatments in preparation of the catalyst have been carried out, it is difficult to determine the relative proportions of Na₂O present in the zeolitic or matrix components, and the overall concentration of Na₂O in the catalyst as well as the concentration in the zeolitic component may be significant in the effectiveness of the catalysts in various conversion processes such as catalytic cracking. Generally, the most effective catalysts are obtained by minimizing the Na₂O concentrations in both zeolite and matrix. Low soda content in the catalyst, particularly in the zeolite component, generally produces greater selectivity for high octane gasoline products in catalytic cracking processes, which is of considerable commercial advantage.

Further, the catalysts of this invention may be provided with a catalytically effective amount of at least one rare earth cation, wherein the term "rare earth cation" is employed to denominate at least one cation selected from the group consisting of cerium, lanthanum, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, lutetium, thulium and ytterbium. The rare earth cation is present in an amount to provide between about 0.1 percent by weight and about 20 percent by weight, expressed as the oxide, based on the total weight of the zeolite component employed in the catalyst, of at least one of the aforementioned rare earth cations. Rare earth cations are preferably present in an amount between about 1 percent by weight and about 12 percent by weight and more preferably in an amount between about 2 percent and about 9 percent by weight, based on the total weight of the large pore zeolite employed in the catalyst.

In this disclosure, including the appended claims, the terms "Na₂O calcination" or characterization of a large pore zeolite or catalyst as "non-calcined" are employed to denominate a thermal treatment of the large pore zeolite (alone or in combination with the inorganic oxide matrix) at an effective temperature to effect a thermal redistribution of cations, e.g., alkali metal cations, associated with the zeolite to promote removal of such by ion exchange. The term "Na₂O calcination" as such applied to Na₂O removal from a zeolite, and is generally understood by those skilled in the art of zeolites to include treatments at temperatures of 300°C or greater for about 1 hour, since at such a temperature and for such a period of time at least some redistribution of the cations associated with the zeolite is effected. For example, in the commercial preparation of catalytic cracking catalysts the zeolite is calcined to a temperature of 500°C or greater to redistribute Na₂O and facilitate ion-exchange of sodium ions in a post-calcination ion exchange. Processes, such as spray drying, which are carried out at temperatures of about 200°C for a period of 5 seconds or less are not considered to come within the scope of the term "Na₂O calcination", since such processes are not carried out to remove cations associated with the zeolite and are of such short duration that no redistribution of the cations associated with the zeolite occurs. Further, a thermal treatment step which is not followed by a cation exchange, e.g., ammonium ion or rare earth cation exchange, is not a "Na₂O calcination" within the meaning of this invention, since such has not been carried out to effect the removal of metal cations, e.g. sodium or other alkali cations associated with the zeolite, and as a result facilitate by thermal means an increase in the ease of ion exchange of such cations. Although a thermal

some extent upon the physical and chemical properties of the particular form of large pore zeolite and the particular inorganic oxide matrix component(s), as well as other process conditions as herein discussed in the instant application. The effective amount of fluoro salt to be added is that amount which achieves a final product having a Na_2O content less than 0.3 percent by weight based on the total weight of the catalyst, or less than 2.0 percent by weight based on the zeolite, without the use of Na_2O calcination step. The effective amount of fluoro salt is preferably greater than 0.0075 moles of fluoro salt per 100 grams of the large pore zeolite, based on the anhydrous weight of the zeolite, and is preferably between about 0.01 and about 0.25. In one embodiment, a Y zeolite is employed and the preferred value of fluoro salt is between about 0.05 to about 0.25 moles of fluoro salt per 100 grams of large pore Y zeolite, based on the anhydrous weight of the Y zeolite.

The effective concentration of the ammonium salt in the ammonium exchange step may be correlated with the temperature and contact time between the mixture of the large pore zeolite and inorganic oxide matrix and the ammonium-containing solutions. Ammonium salt solution having ammonium ion concentrations of from 10^{-3} moles per liter of solution up to saturation can generally be employed herein. The effective amount of ammonium ion is preferably in the range of between about 1.0 and about 20.0 moles per 100 grams of large pore zeolite, on an anhydrous basis, preferably between about 1.0 and about 10.0 and more preferably between about 1.5 and about 8.0 moles of ammonium per 100 grams of large pore zeolite, based on the anhydrous weight. This effective amount of ammonium ion may be provided in a single ion exchange step, but is usually and preferably provided in two or more ion exchange steps. The ammonium salt solutions may be formed from any organic or inorganic species that forms ammonium ions on addition to water. Representative salts are ammonium salts, such as ammonium carboxylates (e.g., acetate), nitrate, sulfate, chloride, bromide, fluoride, carbonate and the like. In one embodiment ammonium ions are provided with the fluoro salt to effect ammonium exchange of the catalyst coincident with the fluoro salt treatment. In this embodiment the ammonium ion concentration is greater than that present as a result of any ammonium ion present as a result of the fluoro salt.

It is desirable that the integrity of the starting zeolite crystal structure be maintained throughout the instant process. The rate of contacting of the mixture of large pore zeolite and inorganic oxide matrix with the fluoro salt is preferably at a rate such that the starting zeolite retains in the final catalyst at least 40, preferably 50, more preferably 60, still more preferably 80, and most preferably at least 90 percent of its original crystallinity. Retention of crystallinity in excess of 80 percent has been observed. Further, the use of fluoro salt solution or slurry having a pH greater than 7 has been observed to provide catalyst products having higher degrees of crystallinity of the zeolite component than those observed for fluoro salt solutions having a pH less than 7. This retention of crystallinity can result in a reduction in the total amount of zeolite which must be employed in the finished catalyst. Fluoro salt solutions having a pH less than about 3 should be avoided as they tend to destroy the crystallinity of the zeolites.

Techniques for measuring crystallinity of zeolites are well known. A convenient technique for assessing the crystallinity of the Y zeolite relative to the crystallinity of the starting Y zeolite is the comparison of the relative intensities of the d-spacings of their respective X-ray powder diffraction patterns. The sum of the peak areas, in terms of arbitrary units above background, of the starting material is used as the standard and is compared with the corresponding area heights of the products. When, for example, the numerical sum of the area heights of the product is 85 percent of the value of the sum of the area heights of the starting zeolite, then 85 percent of the crystallinity has been retained. In practice, it is common to utilize only a portion of the d-spacings for this purpose, as for example, five of the six strongest d-spacings. In zeolite Y, these d-spacings correspond to the Miller Indices 331, 440, 533, 642 and 555. Other indicia of the crystallinity retained by the zeolite product are the degree of retention of surface area and the degree of retention of the adsorption capacity. Surface areas can be determined by the well-known Brunauer-Emmett-Teller method (B-E-T) as described in J. Am. Chem. Soc., 60, 309 (1938) using nitrogen as the adsorbate. In determining the adsorption capacity, the capacity for oxygen at -183°C at 100 Torr is preferred.

The essential X-ray powder diffraction patterns may be obtained using standard X-ray powder diffraction techniques. The radiation source is a high-intensity, copper target, x-ray tube operated at 50 Kv and 40 ma. The diffraction pattern from the copper K-alpha radiation and graphite monochromator is suitably recorded by an X-ray spectrometer scintillation counter, pulse-height analyzer and strip-chart recorder. Flat compressed powder samples are scanned at 2° (2 theta) per minute, using a 2 second time constant. Interplanar spacings (d) are obtained from the positions of the diffraction peaks expressed as 2θ , where θ is the Bragg angle, as observed on the strip chart. Intensities are determined from the heights of diffraction peaks after subtracting background.

INORGANIC OXIDE MATRIX COMPONENTS

The catalysts of the present invention are formed from at least one large pore zeolite and at least one inorganic oxide matrix component. As aforementioned, the large pore zeolite and inorganic oxide matrix component(s) are physically combined prior to the treatment with the fluoro salt solution or slurry, and this has been found to provide numerous advantages.

The inorganic oxide matrix may be a porous alumina matrix having discrete particles of various porous aluminas and/or crystalline aluminas. Porous alumina matrices are generally in the form of discrete particles having total surface areas, as measured by the method of Brunauer, Emmett and Teller (BET), of greater than about 20 square meters per gram (M^2/g), preferably greater than about $40M^2/g$, and more preferably, from about $100 M^2/g$ to about $300 M^2/g$. The pore volume of such alumina matrices will typically be greater than 0.35 cubic centimeters per gram (cc/g). The average particle size of such alumina particles is generally less than 10 microns and preferably less than about 3 microns. The alumina matrix may be preformed and placed in a physical form such that its surface area and pore structure, if any, are stabilized so that when it is added to an impure, inorganic gel containing considerable amounts of residual soluble salts, especially sodium salts, the salts will not alter the surface and pore characteristics measurably nor will they promote chemical attack on preformed porous aluminas. For example, the alumina matrix may be an alumina which has been formed by suitable chemical reaction, slurry aged, filtered, dried, washed substantially free of residual salt, e.g., Na_2SO_4 , and then heated to reduce its volatile content to less than about 15 weight percent. The alumina binder may be present with the zeolite and any other inorganic oxide matrix component in an amount ranging from about 1 to about 99 weight percent and is often present in an amount from about 5 to 90 weight percent, based on the total weight of the finished catalyst. Further, an alumina hydrosol or hydrogel or hydrous alumina slurry may be used initially in the preparation of the catalyst as precursor of the discrete particles of alumina in the final catalyst. British Patent Specification No. 1,315,533, published May 2, 1983, incorporated herein by reference, is representative of an inorganic matrix formed using an alumina sol.

A wide variety of inorganic oxide matrices may be employed in addition to or in substitution of an alumina matrix. Representatives of such matrix systems are disclosed in U. S. Patent Nos. 3,446,727 and 4,086,187, such U.S. Patents being incorporated herein by reference. Accordingly, inorganic oxide matrices which are employable herein include amorphous catalytic inorganic oxides, such as silica, alumina, silica-alumina, silica-zirconia, silica-magnesia, alumina-boria, alumina-titania and the like and mixtures thereof. The use of acid silica and acid alumina sols are representative of silicas and aluminas employed in forming such matrices. The inorganic oxide gel may be an amorphous silica-alumina component such as a conventional silica-alumina cracking catalyst, several types and compositions of which are commercially available. These materials are generally prepared as a cogel of silica and alumina or as alumina precipitated on a preformed and preaged hydrogel. U.S. Patent No. 4,086,187 is representative of an inorganic matrix formed using an acid silica sol. The silica may be present as a component in the solids present in said gels in an amount between about 10 and about 99 weight percent and often between about 20 and about 90 weight percent. The silica may also be employed in the form of a cogel comprising about 75 weight percent silica and about 25 weight percent alumina or comprising about 87 weight percent silica and about 13 weight percent alumina.

Another method of preparing such catalysts employing silica-alumina and porous alumina is to react sodium silicate with a solution of aluminum sulfate to form a silica/alumina hydrogel slurry which is then aged to give the desired pore properties, filtered to remove a considerable amount of the extraneous and undesired sodium and sulfate ions and then reslurried in water. The alumina may be prepared by reacting solutions of sodium aluminate and aluminum sulfate under suitable conditions, aging the slurry to give the desired pore properties of the alumina, filtering, drying, reslurrying in water to remove sodium and sulfate ions and drying to reduce volatile matter content to less than 15 weight percent. The alumina may then be slurried in water and blended in proper amounts with a slurry of impure silica-alumina hydrogel. The zeolite component(s) may then be added to this blend. A sufficient amount of each component is utilized to give the desired final composition. The resulting mixture is then filtered to remove a portion of the remaining extraneous soluble salts therefrom. The filtered mixture is then dried to produce dried solids. The dried solids are subsequently reslurried in water and washed substantially free of the undesired soluble salts.

The catalyst may then be dried to a residual water content of less than about 15 weight percent.

The inorganic oxide matrix component will typically be present in the catalyst in an amount between about 10 and about 99 weight percent, preferably between about 30 and about 80 weight percent, based on the total catalyst. It is also within the scope of the instant invention to employ other materials with the final cracking catalysts, including various other types of molecular sieves, e.g., aluminophosphates,

silicocaluminophosphates and zeolites, clays (such as kaolin clay), carbon monoxide oxidation promoters, etc.

It is anticipated that the catalyst in most instances will include between about 5 and about 40 weight percent of a large pore zeolite and a clay component, preferably a kaolin clay, in an amount between about 30 and about 35 percent by weight based on the total weight of the catalyst. The preferred catalysts will contain between about 10 and about 25 weight percent of a large pore zeolite, preferably a Y zeolite, and between about 5 percent by weight and about 25 percent by weight of a silica and/or an alumina component, and between about 45 percent by weight and about 75 percent by weight of a clay, preferably kaolin clay, such weights being based on the total weight of the catalyst.

The finished catalyst, formed of at least one large pore zeolite and at least one inorganic oxide matrix component, may be formed into the final form for the catalyst by standard catalyst forming techniques. Such catalysts are generally formed by spray drying procedures, such procedures being well known in the art, or may be formed as extruded pellets. Catalysts may be extruded through a one eighth inch extruder to form pellets and the pellets dried at about 110°C. The extruded pellets may be dried in an air purge, e.g., at a programmed temperature increased from room temperature to about 220°C over a 1.5 hour period, and may be further then heated to 480°C over a period of 1.5 hour and held at 480°C for 1.5 hour if desired. Such pellets may then be crushed and sized to the desired particle size, e.g., less than 150 microns.

The combination of the large pore zeolite and the inorganic oxide matrix may be exchanged with ammonium and/or other cations before treatment with the fluoro salt. Such ion-exchange steps are generally carried out by slurrying the mixture of zeolite and/or inorganic oxide matrix with between 5 to 15 volumes of water per the volume of large pore zeolite and/or inorganic oxide matrix after which a salt of the selected cation, e.g., ammonium or rare earth cations, may be added to the slurry. The resulting mixture is typically heated to a temperature above about 50°C for a period between about 0.5 hours and about 3 hours. The mixture is then filtered and water-washed until excess anion is removed. The process is typically repeated one or more times according to the above described procedure. Techniques for the ion-exchange of matrixed catalysts are disclosed in U.S. Patent No. 3,930,987, incorporated herein by reference thereto, and such are generally employable herein.

The instant catalysts are well suited for use in all types of catalytic cracking processes. Such processes can be conducted in any conventional catalytic cracking manner by employing the cracking catalysts of the instant invention. The catalysts of this invention are particularly applicable to fluid catalytic cracking (FCC) processes. Suitable catalytic cracking conditions include a temperature ranging from about 400°F. to about 1300°F., preferably from about 700°F. to about 1300°F., more preferably from about 900°F. to about 1100°F., and a pressure ranging from subatmospheric to about superatmospheric pressure, typically from about atmospheric to about 100 psig. The process may be carried out in a fixed bed, moving bed, ebulliating bed, slurry transfer line, riser unit, batchwise or fluidized bed operation. The catalysts of the present invention can be used to convert any of the conventional hydrocarbon feeds used in catalytic cracking, e.g., crude oil-derived feedstocks, that is, it can be used to crack naphthas, gas oils and residual oils, including those having a high content of metal contaminants. It is especially suited for cracking hydrocarbons boiling in the gas oil range, that is, hydrocarbon oils having an atmospheric pressure boiling point ranging from about 450°F. to about 1100°F. to naphthas to yield not only products having a lower boiling point than the initial feed but also products having an improved octane number. Hydrocarbon fractions employable herein include gas oils, residual oils, cycle stocks, whole top crudes and heavy hydrocarbon fractions derived by the destructive hydrogenation of coal, tar pitches, asphalts and the like.

EXAMPLES

The present invention is illustrated by the following non-limiting examples:

Examples 1 to 7

Catalysts were formed by preparing catalyst formulations having the following relative proportions on a dry weight basis:

Component	Weight Percent
Zeolite Y (Y-52)	18
SiO ₂	20
Kaolin clay	62

The SiO₂ source was an acid silica sol prepared using an aqueous acid solution prepared from 9.4 percent mineral acid, buffered to a pH of about 3. The mixture was then cooled to room temperature (18°C - 22°C). This mixture was mixed with a 53 weight percent aqueous solution of Na₂SiO₃ by pumping the two solutions through a mixer. The relative flow rates of the two solutions were adjusted to maintain the pH of the product at about 2.8 and solid products, if any, were removed as formed.

The catalysts were formed by adding the kaolin clay component to the acid silica sol containing 6.3 percent by weight SiO₂ in water. The mixture was blended for about 10 minutes. The zeolite Y was added to this mixture with enough water to give a slurry having 25 percent by weight solids. The pH of the mixture was adjusted to less than 4.5 (4.3-4.4) by addition of sulfuric acid. The mixture was then mixed for 10 minutes. The mixture was then spray dried at 175°C (contact time less than about 5 seconds) and the product sized to exclude particles greater than 150 microns. The final catalyst had an average particle size of about 64 microns.

The spray dried mixture was then employed to form a catalyst using one of the following methods.

Method A

The spray dried mixture of zeolite, SiO₂ and kaolin clay is employed to form a catalyst by preparing a slurry of 500 grams of the mixture in 4 liters of water at 75°C. The slurry is mixed for 5 minutes and filtered. The filtered solid is reslurried in 4 liters of a (NH₄)₂SO₄ solution at 75°C where the solution is prepared by dissolving 200 grams of (NH₄)₂SO₄ in 4 liters of distilled water. The slurry was mixed for 30 minutes. A 10 percent by weight solution of ammonium hexafluorosilicate solution was added to the slurry by adding 168 milliliters dropwise over a period of one hour. The mixture was then cooled to 50°C. To this mixture there was added 54.2 grams of Al₂(SO₄)₃. The resulting mixture was mixed for two hours, filtered, the solid product washed with 2 liters of distilled water at 50°C and filtered, and then the solid product was slurried at 50°C in 4 liters of an (NH₄)₂SO₄ solution (160 grams of (NH₄)₂SO₄ in 4 liters of H₂O), mixed for 10 minutes and filtered. The solid product was then washed with 4 liters of distilled water at 50°C and filtered. The previous step is repeated two additional times except that instead of washing the solid product with 4 liters of distilled water the product is washed with 10 liters of water at 50°C which has had the pH adjusted to 9.0 by addition of NH₄OH. The wash liquid is tested for sulfate anions and washing continued until sulfate was not qualitatively detected (less than about 500 ppm). The final solid product was either air dried for 10 to 24 hours or was dried overnight (6 hours to 12 hours) at 100°C in air.

Method B

Method B is similar to Method A except that the mixture of zeolite Y, silica and kaolin clay was treated with an aqueous (NH₄)₂SO₄ solution after the slurry was filtered and before reslurry of the filtered solid with the 4 liters of (NH₄)₂SO₄ solution. This ((NH₄)₂SO₄ treatment step was carried out similar to the final (NH₄)₂SO₄ treatment steps employed in Method A. Further, the final treatment step of Method A involving (NH₄)₂SO₄ was carried out only twice instead of the three times of Method A.

The catalyst prepared in example 1 was analyzed for Na₂O, SiO₂ and Al₂O₃. In addition, spray dried samples were analyzed of: 1) a mixture of zeolite Y (sodium form), the kaolin clay and the SiO₂, as employed in examples 1 to 19; and 2) of the kaolin clay and SiO₂. The chemical analyses were as follows:

Sample	Na ₂ O	SiO ₂	Al ₂ O	Na ₂ O*
Example 1	0.1	66.34	30.1	-
NaY zeolite	8.4	57.22	3.11	6.98
Kaolin Clay	5.9	55.9	31.6	5.9

* Percent of reported Na₂O present as Na₂SO₄.

The catalysts of examples 1 to 7 were evaluated by microactivity tests (MAT) according to ASTM test method D-3907 employing a feedstock having an API gravity of 24.0°, an IBP (Initial Boiling Point) of 354° F, a FBP (Final Boiling Point) of 1077° F and a UOP K Factor of 11.8. The UOP K Factor is defined as

$$K = \frac{(T_B)^{1/3}}{d}$$

where "T_B" is the average boiling point in degrees Rankine and "d" is the specific gravity 60°/60° F. The percent coke, selectivity to gasoline products and percent conversion are set forth in Table I. Gasoline products are hydrocarbon products containing C₅ hydrocarbons (boiling at about 110° F) to hydrocarbons boiling at or below 430° F. Coke refers to hydrocarbons which are adsorbed by the catalysts and are not removed by stripping.

TABLE I

Example	Steaming Temperature (F) ¹	Method	Rare Earth ²	Na ₂ O	% Coke	% Gasoline Selectivity ³	Percent Conversion ³
1	1450	B	0	0.14	0.51	79.2	49.5
2	1450	A	0.75	0.21	0.57	79.2	59.4
3	1450	B	0.75	0.13	0.88	77.6	59.3
4	1450	A	2.7	0.21	0.82	79.2	57.9
5	1450	B	1.95	0.13	0.73	76.3	62.5
6	1500	A	0	0.23	0.62	77.0	57.8
7	1450	A	0.5	0.21	0.47	77.2	55.9

1 All catalysts were steamed prior to testing by employing 100% steam (weight basis) for 2 hours.

2 Weight percent based on total catalyst weight.

3 % Conversion is defined in ASTM test method D-3907. % Gasoline is the (weight of gasoline product/weight of feedstock)/(Percent Conversion). % Coke is the (weight of coke)/(weight of feedstock).

Example 8

A catalyst was prepared according to Method B as above described, to show that a catalyst treated only with an equivalent molar amount of ammonium sulfate solution, as obtained by use of the ammonium fluoro salt solutions and ammonium sulfate solutions employed in Examples 1-7, does not provide a catalyst having a final Na₂O content less than 0.3 percent by weight, based on the total catalyst weight. The catalyst was prepared according to Method B by substituting a solution of ammonium sulfate containing an equivalent molar amount of ammonium ion for the ammonium hexafluorosilicate and aluminum sulfate solution employed in Method B. The final catalyst contained 0.412 weight percent Na₂O and zero weight percent rare earth, expressed as the oxide.

These results demonstrate the importance of preparing the catalyst according to this invention by treatment of the large pore zeolite and inorganic oxide matrix with a fluoro salt and not simply with

ammonium-containing solutions.

Examples 9 to 11

Three catalysts were prepared as in examples 1 to 7, according to Method B, except that quantities of 10, 30 and 40 percent by weight of the zeolite Y component, respectively, in examples 9, 10 and 11, were employed instead of the 18 percent by weight employed in examples 1 to 7. A portion of the clay component was added or removed to compensate for the change in the weight percent of the zeolite component. The catalysts were not treated with rare earth cations. Contents of Na₂O comparable to the catalysts of Table I were obtained.

The three catalysts were steam deactivated in 100 percent steam (volume basis) for 2 hours at the temperatures set forth in Table II and when two temperatures were employed such were denominated as Runs A or B. The catalysts were evaluated according to the procedure employed for examples 1 to 7 and the following results obtained, as shown in Table II:

TABLE II

Example	Run	Temp (°F)	% Na ₂ O	Coke*	% Gasoline Selectivity*	% Conversion*
9	A	1450	0.16	0.59	70.9	44.5
10	A	1450	0.25	0.95	71.9	63.5
10	B	1550	0.25	0.40	80.3	44.2
11	A	1450	0.15	1.12	74.3	70.7
11	B	1550	0.15	0.56	72.7	56.0

*As defined in Table I

Example 12

A catalyst was prepared according to Method B except that the 18 weight percent Y-52 was replaced by 18 weight percent LZ-210 (silica-to-alumina ratio of 6.5) containing 2.5 weight percent Na₂O based on the weight of LZ-210 and zero percent by weight rare earth. The catalyst was treated at 1450 °F in 100 percent steam for 2 hours and evaluated by the procedure employed for examples 1 to 7. The results of the evaluation and of the % Gasoline Selectivity and % Coke were as follows:

% Conversion	:	53.1
% Gasoline Selectivity	:	73.5
% Coke	:	0.82

Example 13

A catalyst was prepared according to Method B, except that the pH of the catalyst slurry was maintained at pH 7 by continuous addition of 20 weight percent aqueous NH₄OH during the addition of the fluoro salt. The catalyst contained 0.39 percent by weight Na₂O, based on the weight of the finished catalyst. The catalyst was treated in 100 percent steam for 2 hours at 1450 °F.

The catalyst was evaluated according to ASTM test method D-3907 as described for examples 1 to 7 and the % Conversion and % Gasoline Selectivity were as follows:

% Conversion	:	59.9
% Gasoline Selectivity	:	74.6

5

Example 14

10 A catalyst was prepared as in examples 1 to 7, according to Method B, except the addition of aluminum sulfate was omitted. Two portions of the catalyst were treated in 100 percent steam for 2 hours at 1450 °F and 1550 °F, respectively. The catalyst was evaluated according to ASTM test method D-3907 as described for examples 1 to 7 and gave the following results:

15

Catalyst Portions	1	2
Deactivation Temp. (°F)	1450 °F	1550 °F
% Conversion	42.5	39.5
% Gasoline Selectivity	78.3	82.3
% Coke	0.43	0.39
% Na ₂ O*	0.13	0.13
% RE ₂ O ₃ *	0	0

20

*based on total catalyst weight

25

Example 15

30

A catalyst was prepared as in examples 1-7 according to Method B except that the ammonium fluorosilicate was replaced by (NH₄)₂TiF₆. The amount of (NH₄)₂TiF₆ employed was that amount required to furnish sufficient titanium to substitute 27.5% of the framework aluminum atoms if 100 percent substitution of TiO₂ tetrahedra for AlO₂ tetrahedra occurred. The catalyst was not rare earth exchanged. Chemical analysis of the product gave the following:

35

	Weight Percent
SiO ₂	63.4
Al ₂ O ₃	30.11
Na ₂ O	0.22
TiO ₂	3.55

40

45

The catalyst was steam (100%) deactivated at 1450 °F for 2 hours and evaluated according to the procedure employed for examples 1 to 7. The results were as follows:

50

% Conversion	:	59.2
% Gasoline Selectivity	:	75.7

55

Examples 17 to 25 and Comparative Example A

Example 16

A catalyst was prepared as in example 12, except that the solution of ammonium hexafluorosilicate and aluminum sulfate was replaced as described in example 20. Six portions of the catalyst (Runs A to F) were evaluated by rare earth exchanging the samples to a given rare earth content and by treatment of the catalysts in 100 percent steam for 2 hours at 1450° F, 1500° F or 1550° F. The catalysts were evaluated according to the procedure employed for examples 1 to 7 and gave the following results as shown in Table III. If these results are compared to those shown in Tables I and II, it can be seen that the methods of catalyst preparation utilizing the fluoroanion solutions produced catalysts having comparable catalytic activity, but much lower Na₂O contents, which would be expected to improve their selectivity for high octane gasoline products.

TABLE III

Run	Temp (° F)	% Na ₂ O ¹	% RE ₂ O ¹	% Coke ²	% Gasoline Selectivity	% Conversion
A	1450	0.47	0.75	0.7	75.6	63.7
B	1500	0.47	0.75	0.4	80.5	47.2
C	1550	0.47	0.75	0.2	58.3	6.9
D	1450	0.47	2.5	0.94	71.1	56.6
E	1500	0.47	2.5	0.58	73.4	47.5
F	1500	0.47	2.5	0.19	72.1	14.2

1 Based on total weight of the catalyst.

2 As defined in Table I.

Additional examples were carried out using catalysts prepared by:

Method C

Method C is similar to Method A except that during the dropwise addition of ammonium hexafluorosilicate to the slurry, the pH of the slurry was maintained at pH 8 by addition of a 20 percent by weight aqueous solution of NH₄OH by constant addition of the NH₄OH. The step of slurrying with (NH₄)₂SO₄, mixing, filtering and washing was repeated only once rather than twice.

When a catalyst was rare earth cation exchanged the rare earth exchange was carried out with a solution containing several rare earth chlorides in amounts sufficient to provide the desired rare earth contents. The rare earth chloride solution employed was obtained from Molycorp, Inc., sold under Product No. 5240, and was the following chemical analyses, expressed as the oxides:

	Weight Percent
La ₂ O ₃	60.0
Nd ₂ O ₃	21.5
CeO ₂	10.0
Pr ₂ O ₃	7.5
Other RE ₂ O ₃	1.0

The rare earth chloride-containing solution was added to a slurry of the catalyst which had been adjusted to about pH 4.5 with acid.

Examples 17 to 21

Four catalysts were prepared as described above. The catalysts were steam deactivated (100% steam) for 2 hours to simulate the deactivation of cracking catalysts occurring in commercial cracking operation. The catalysts were chemically analyzed and were evaluated by microactivity testing (MAT) according to ASTM test method D-3907 as described above. The chemical analysis, percent coke, percent gasoline selectivity and percent conversion are set forth in Table IV. The Percent (%) Conversion is as defined in ASTM test method D-3907. The percent gasoline selectivity is the (weight of gasoline product/weight of feedstock)/(%Conversion). The % Coke is the (weight of coke)/(weight of feedstock). Gasoline products are hydrocarbon products containing from C₅ hydrocarbons (boiling at 110° F) to hydrocarbons boiling at 430° F. Coke refers to hydrocarbons which are absorbed by the catalysts and not removed by stripping.

Table IV

Example	Steam Deactivation Temperature (° F)	Na ₂ O ¹	RE ₂ O ₃ ¹	% Coke	% Gasoline Selectivity	% Conversion
17	1450	0.31	0.66	1.19	71.9	67.4
18	1550	0.31	0.66	0.79	76.9	56.7
19	1450	0.29	1.98	1.49	66.6	73.3
20	1550	0.29	1.98	0.98	75.2	61.6
21	---	0.34	0	---	---	---
22	1550	0.24	0	0.70	77.1	61.6
23	1450	0.30	0	0.79	75.6	57.4
A	1450	0.13	1.95	0.73	76.3	62.5

¹ Weight percent based on total catalyst weight.

Example 22

The above catalyst preparation procedure C for catalysts 17 to 21 was repeated, except that no Al₂(SO₄)₃ was added after treatment with the ammonium fluorosilicate solution. The result of the chemical analysis of the product for Na₂O is also set forth in Table IV.

Example 23

The above catalyst preparation procedure C for catalysts 17 to 21 was repeated, except that the ammonium fluorosilicate and aluminum sulfate solution was added in one step instead of over a period of time. The pH of the solution was adjusted to pH 8 by use of NH₄OH before addition to the zeolite slurry and the pH of the slurry was adjusted to pH 8 by use of NH₄OH after mixture. The chemical analysis of the product and evaluation according to ASTM Test Method D-3907, as employed for examples 16 to 20 are also set forth in Table IV.

Comparative Example A

This is a comparative example where a catalyst was prepared as in examples 16 to 20 except that the pH of the slurry was less than pH 7 (approximately pH 5 to 6). The results of the evaluation of the product, as shown in Table IV, show that the product was less active than a product having similar rare earth content, as shown by comparison to example 19. The catalyst was evaluated according to the procedure employed for examples 16 to 20 after steam deactivation at 1450° F. Surprisingly, the high pH treatment results in a product containing a slightly higher Na₂O content and exhibits a higher Na₂O tolerance in the finished catalyst while still providing an active catalyst.

Example 24

A catalyst was prepared according to the procedure of examples 17 to 21, except that the catalyst was treated with an equivalent molar amount of an ammonium sulfate solution instead of with the ammonium fluorosilicate whereby the ammonium sulfate solution contained an equivalent molar amount of ammonium ion as compared to that which was obtained by use of the ammonium hexafluorosilicate solution employed. A catalyst was prepared as in examples 17 to 21 except that no rare earth exchange was carried out. The final catalyst contained 0.412 weight percent Na_2O and zero weight percent rare earth.

These results demonstrate the importance of preparing the catalyst according to this invention by treatment of the large pore zeolite and inorganic oxide matrix with a fluoro salt and not simply by ammonium exchanging the zeolite-matrix composite.

Example 25

A catalyst was prepared by forming a slurry by mixing 200 grams of the zeolite Y, SiO_2 and kaoline clay spray dried mixture employed in forming the catalysts in examples 17 to 21 in 2 liters of water at 75°C . The mixture was filtered and the filtered solid added to two liters of a 4 percent by weight aqueous solution of $(\text{NH}_4)_2\text{SO}_4$ to form a slurry. The slurry was blended for 10 minutes, filtered and the solid product washed with 1 liter of water. The solid product was again slurried in 2 liters of the $(\text{NH}_4)_2\text{SO}_4$ solution, filtered and the solid product washed with water as above described. The solid product was slurried in two liters of a 4 percent by weight aqueous solution of $(\text{NH}_4)_2\text{SO}_4$. The slurry was mixed for 30 minutes and the pH of the slurry adjusted to about 7.5 by addition of NH_4OH . To this slurry was added 0.034 liters of a 10 percent by weight aqueous solution of ammonium fluorosilicate. The solution was added in a single addition step. The pH of the slurry was readjusted to 7.5 by addition of NH_4OH and the slurry maintained at pH 7.5 by addition of NH_4OH , as required, for 30 minutes. The slurry was cooled to 50°C . 21.7 grams of $\text{Al}_2(\text{SO}_4)_3$ added to the slurry mixed for 2 hours. The slurry was filtered and the solid product washed with 1 liter of water. The solid product was added to 2 liters of water. The solid product was added to 2 liters of a 4 percent by weight aqueous solution of $(\text{NH}_4)_2\text{SO}_4$, mixed for 10 minutes and filtered. The solid product was washed with 1 liter of water. The solid product was then washed with 10 liters of water having a pH of 9, formed by addition of NH_4OH . Two samples of the final product were steam deactivated at 1450°F and 1550°F , in 100 percent steam for 2 hours. The steam deactivated solid products were evaluated by ASTM test method D-3907 and the percent conversion measured. The gasoline selectivity and percent coke were calculated. The results were as follows:

	Steam Deactivation Temperature	
	1450°F	1550°F
% Conversion	72.1	56.3
% Gasoline Selectivity	70.7	78.4
% Coke	1.17	0.67

Claims

1. A process for the catalytic conversion of hydrocarbons under effective conversion conditions wherein said process employs as the catalyst at least one catalyst of U.S. Patents Nos. 4,588,701 and 4,591,576.

2. The process for catalytic cracking of crude oil-derived feedstocks comprising contacting said feedstock under effective cracking conditions with at least one catalyst of U.S. Patents Nos. 4,588,701 and 4,591,576.

3. A process for the catalytic cracking of hydrocarbon feedstocks comprising contacting said hydrocarbon feedstock under conditions effective to crack said feedstock with a catalyst prepared by the following steps:

(i) contacting a mixture of a large pore zeolite and an inorganic oxide matrix with a fluoro salt of the formula

5 $A_{n-m}(MF_n)_z$

wherein "A" is an organic or inorganic ionic moiety; $(MF_n)_z$ is a fluorocanion moiety comprising the element "M". "M" is an element selected from the group of elements from Groups VB, VIB, VIIB, VII, IIIA, IVA and VA of the Periodic Table of Elements; "n" is the coordination number of "M"; "m" is the valence of "M"; and "z" is the valence or charge associated with "A"; at an effective pH value greater than about 3, at effective conditions of temperature and time, whereby the cracking activity of the zeolite is enhanced.

4. The process according to claim 3 wherein said catalyst is prepared by the following steps:

(i) contacting a mixture of Y zeolite having a SiO_2/Al_2O_3 ratio of between about 3.5 and about 6, and an inorganic oxide matrix, said matrix comprising a mixture of a kaolin clay and at least one of silicas, aluminas and silica-aluminas, with a fluoro salt selected from the group consisting of ammonium hexafluorosilicate, ammonium hexafluorotitanate and mixtures thereof in an amount of at least 0.0075 moles per 100 grams of zeolite, at effective conditions of temperature and time whereby at least one of silicon and titanium is inserted as tetrahedral units into the crystal lattice of the zeolite in substitution for aluminum tetrahedra; and

(ii) ammonium exchanging the product of step (i) to provide a catalyst having a Na_2O content less than 0.3 percent by weight based on the total catalyst weight.

5. The process of claim 3 wherein the effective pH is between 3 and 7.

6. The process of claim 3 wherein the pH is between about 4.0 and about 6.5.

7. The process of claim 3 wherein the effective pH is greater than about 7.

8. The process of claim 7 wherein the effective pH is between 7.5 and about 9.0.

9. The process of claim 7 wherein the effective pH is between about 7.5 and about 8.5.

10. The process according to claim 3 comprising the additional steps of ammonium exchanging the product of step (i) to provide a catalyst having a Na_2O content less than 0.3 percent by weight, based on the total catalyst weight.

11. The process according to claim 3 comprising the additional preparation steps of ammonium exchanging the product of step (i) to provide a catalyst having a Na_2O content less than 2.0 percent by weight, based on the total weight of the zeolite employed in such catalyst, wherein such Na_2O content is achieved without a Na_2O calcination.

12. The process of claim 3 or claim 10 or claim 11 wherein the product of step (i) is cation exchanged with a catalytically effective amount of at least one rare earth cation selected from the class consisting of cerium, lanthanum, praseodymium, neodymium, promethium, samarium, europium, lutetium, gadolinium, terbium, dysprosium, holmium, erbium, thulium and ytterbium.

13. The process of claim 3 wherein said large pore zeolite is a Y zeolite having a SiO_2/Al_2O_3 ratio greater than about 3.5.

14. The process according to claim 13 wherein said Y zeolite has a SiO_2/Al_2O_3 ratio between about 4.0 and about 6.5.

15. The process according to claim 13 wherein said Y zeolite is at least partially in the ammonium cationic form.

16. The process of claim 3 wherein the effective temperature is at least 50 °C.

17. The process of claim 16 wherein the effective temperature is between about 50 °C and about 100 °C.

18. The process of claim 3 wherein the effective time is between about 0.1 hours and about 2 hours.

19. The process of claim 3 wherein the fluoro salt is provided in an amount greater than 0.0075 moles per 100 grams of large pore zeolite.

20. The process of claim 19 wherein the fluoro salt is provided in an amount between about 0.05 and about 0.2 moles per 100 grams of large pore zeolite.

21. The process of claim 3 wherein the fluoro salt is provided in an amount between about 0.01 and about 1.25 moles per 100 grams of large pore zeolite.

22. The process of claim 21 wherein the fluoro salt is provided in an amount between about 0.02 and about 0.25 moles per 100 grams of large pore zeolite.

23. The process of claim 10 wherein the catalyst contains less than 0.2 percent by weight Na_2O based on the total weight of the catalyst.

24. The process of claim 23 wherein the catalyst contains less than 0.1 percent by weight Na_2O based on the total weight of the catalyst.

25. The process of claim 11 wherein the catalyst contains less than 1.5 percent by weight Na_2O , based on the total weight of the large pore zeolite.

5 26. The process of claim 25 wherein the catalyst contains less than 1.0 percent by weight Na_2O based on the total weight of the large pore zeolite.

27. The process of claim 3 wherein the inorganic oxide matrix is selected from the group consisting of silicas, aluminas, silica-aluminas, clays and mixtures thereof.

28. The process of claim 27 wherein the zeolite and inorganic oxide matrix comprise a mixture of
10 between about 5 and about 40 percent by weight of the large pore zeolite, 10 percent and about 25 percent by weight of at least one of silica and alumina and between about 45 percent and about 75 percent of clay.

29. The process of claim 28 wherein the zeolite and inorganic oxide matrix comprise a mixture of between about 10 and about 25 percent by weight of at least one of silica and alumina and between about 45 percent and about 75 percent of a kaolin clay.

15 30. The process of claim 28 wherein the zeolite is zeolite Y, the silica is an acid silica sol and the clay is a kaolin clay.

31. The process of claim 28 wherein the alumina is an acid alumina sol.

32. The process of claim 29 wherein the zeolite is present in an amount of between about 15 and about 20 percent by weight, based on the total weight of the catalyst.

20 33. The process of claim 12 wherein the final product contains less than 0.2 percent by weight Na_2O , based on the total weight of the catalyst, and between about 0.1 and about 20 weight percent of at least one rare earth cation, based on the weight of zeolite.

34. The process of claim 12 wherein the final product contains less than 2.0 percent by weight Na_2O , based on the total weight of the zeolite, and between about 1 and about 12 weight percent of at least one
25 rare earth cation, based on the weight of zeolite.

35. The process of claim 3 wherein at least 40 percent of the crystallinity of the starting large pore zeolite is retained by the zeolite in the catalyst.

36. The process of claim 3 wherein said large pore zeolite is selected from the group consisting of zeolite Y, zeolite X, zeolite beta, zeolite ZK-20, Zeolite LZ-210, Zeolite ZSM-3, ZSM-type zeolites and
30 mixtures thereof.

37. The process of claim 36 wherein said zeolite is a mixture of a Y zeolite and LZ-210.

38. The process of claim 36 wherein said zeolite is Zeolite beta.

39. The process of claim 36 wherein said zeolite is Zeolite ZK-20.

40. The process of claim 36 wherein said zeolite is ZSM-3.

35 41. The process of claim 36 wherein said zeolite is LZ-210.

42. The process of claim 3 wherein "M" is selected from the group consisting of silicon, phosphorus, antimony, bismuth, palladium, platinum, iridium, iron, rhenium, molybdenum, tantalum, titanium and mixtures thereof.

43. The process of claim 36 wherein said zeolite comprises a ZSM-type zeolite selected from the group
40 consisting of ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38 and ZSM-48.

44. The process of claim 42 wherein "M" is selected from the group consisting of silicon, titanium and mixtures thereof.

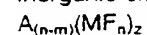
45. The process of claim 3 wherein "A" is selected from the group consisting of cations of ammonium, quaternary ammonium and mixtures thereof.

46. The process of claim 44 wherein the fluoro salt is ammonium hexafluorosilicate.

47. The process of claim 4 wherein said catalyst is prepared in the absence of a Na_2O calcination.

48. A process for catalytic cracking of hydrocarbon feedstock comprising contacting said hydrocarbon feedstock under conditions effective to crack said feedstock with a catalyst prepared by the following steps:

(i) contacting a mixture of a Y zeolite having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio between about 3.5 and 6 and an
50 inorganic oxide matrix with a fluoro salt of the formula



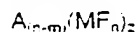
wherein "A" is an organic or inorganic ionic moiety; $(\text{MF}_n)_z$ is a fluoroanion moiety comprising the element "M"; "M" is an element selected from the group of elements from Groups VB, VIB, VIIB, VIII, IIIA, IVA, and VA of the Periodic Table of Elements; "n" is the coordination number of "M"; "m" is the valence of "M";
55 and "z" is the valence or charge associated with "A"; at a pH from 3 to about 7 in an amount of at least 0.0075 moles per 100 grams of the large pore zeolite on an anhydrous basis, whereby the cracking activity of the zeolite is enhanced;

(ii) ammonium exchanging the product of step (i) to provide a catalyst having a Na_2O content less than 0.3 percent by weight, based on the total catalyst weight; and

(iii) with the proviso that such process is carried out in the absence of a Na_2O calcination of said Y zeolite.

49. The process for catalytic cracking of hydrocarbon feedstock comprising contacting said hydrocarbon feedstock under conditions effective to crack said feedstock with a catalyst prepared by the steps of:

(i) contacting a fluoro salt with a mixture of a large pore zeolite selected from the class consisting of zeolite Y, zeolite X, zeolite beta, zeolite LZ-210, zeolite ZK-20, zeolite ZSM-3 and mixtures thereof and an inorganic oxide matrix selected from the group consisting of aluminas, silicas, silica-aluminas, clays, and mixtures thereof, wherein the fluoro salt is of the formula:



wherein "A" is an organic or inorganic ionic moiety; $(\text{MF}_n)_z$ is a fluoroanion of element "M"; "M" is at least one of boron, aluminum, gallium, silicon, phosphorus, antimony, bismuth, palladium, platinum, iridium, iron, rhodium, molybdenum, tantalum and titanium; "n" is the coordination number of "M"; "m" is the valence of "M"; and "z" is the valence or charge associated with "A"; at an effective pH value within the range of about 3 to about 7 for an effective time at an effective temperature whereby the cracking activity of the zeolite is enhanced;

(ii) ammonium exchanging the product of step (i);

(iii) rare earth exchanging the product of step (iii);

(iv) obtaining without Na_2O calcination a catalyst containing less than 0.3 weight percent Na_2O , based on the total catalyst weight, and about 20 weight percent of at least one rare earth element cation selected from the group consisting of cerium, lanthanum, praseodymium, neodymium, promethium, samarium, europium, lutetium, gadolinium, terbium, dysprosium, holmium, erbium, thulium and ytterbium, based on the total weight of the zeolite.

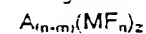
50. A process for the catalytic cracking of a hydrocarbon feedstock comprising contacting said feedstock under conditions effective to crack said feedstock with a cracking catalyst prepared by the following process:

(i) contacting a mixture of a non-calcined Y zeolite having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of between about 3.5 and about 6, and at least one inorganic oxide matrix component, said matrix comprising a mixture of a kaolin clay and at least one of silicas, aluminas, silica-aluminas, with a fluoro salt selected from the group consisting of ammonium hexafluorosilicate, ammonium hexafluorotitanate and mixtures thereof in an amount of at least 0.0075 moles per 100 grams of Y zeolite, at an effective pH value of from greater than 7 to about 9 at effective conditions of temperature and time whereby the cracking activity of the zeolite is enhanced; and

(ii) ammonium exchanging the product of step (i) to provide a catalyst having a Na_2O content less than 2.0 percent by weight based on the total weight of the Y zeolite employed in the catalyst.

51. A process for the catalytic conversion of a hydrocarbon feedstock comprising contacting said feedstock under conditions effective to crack said feedstock with a non-calcined catalyst having a Na_2O content less than 2.0 percent by weight, based on the zeolite component of the catalyst, wherein said catalyst is prepared by the following steps:

(i) contacting a mixture of a Y zeolite having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio between about 3.5 and 6 and an inorganic oxide matrix with a fluoro salt of the formula

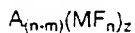


wherein "M" is an organic or inorganic ionic moiety; $(\text{MF}_n)_z$ is a fluoroanion moiety comprising the element "M"; "M" is an element "M"; "M" is an element selected from the group of elements from Groups VB, VIB, VIIB, VIII, IIIA, IVA and VA of the Periodic Table of Elements; "n" is the coordination number of "M"; "m" is the valence of "M"; and "z" is the valence or charge associated with "A"; at a pH from 7.5 to about 9 in an amount of at least 0.0075 moles per 100 grams of the large pore zeolite on an anhydrous basis, whereby the cracking activity of the zeolite is enhanced;

(ii) ammonium exchanging the product of step (i) to provide a non- Na_2O calcined catalyst having a Na_2O content less than 2.0 percent by weight, based on the total weight of the Y zeolite employed in the catalyst.

52. A process for the catalytic cracking of a hydrocarbon feedstock comprising contacting said feedstock under conditions effective to crack said feedstock with a catalyst prepared by the process consisting essentially of the steps of:

- (i) contacting a mixture of a large pore zeolite selected from the class consisting of zeolite Y, zeolite X, zeolite beta, zeolite LZ-210, zeolite ZK-20, zeolite ZSM-3 and mixtures thereof and an inorganic oxide matrix component selected from the group consisting of aluminas, silicas, silica-aluminas, clays, and mixtures thereof with a fluoro salt, wherein the fluoro salt is of the formula



- wherein "A" is an organic or inorganic ionic moiety; $(MF_n)_z$ is a fluoropositive of element "M"; "M" is at least one of boron, aluminum, gallium, silicon, phosphorus, antimony, bismuth, palladium, platinum, iridium, iron, rhenium, molybdenum, tantalum, and titanium; and "z" is the valence or charge associated with "A" at an effective pH greater than 7 for effective conditions of time and temperature whereby the cracking activity of the zeolite is enhanced;

(ii) ammonium exchanging the product of step (i);

- (iii) rare earth exchanging the product of step (ii) to provide a catalytically effective amount of rare earth cation;

- (iv) obtaining without Na_2O calcination a product containing less than 1.2 weight percent Na_2O , based on the weight of the zeolite employed in the catalyst, at least 60 percent crystal retention of the starting zeolite and between about 0.1 and about 20 weight percent of at least one rare earth element cation selected from the group consisting of cerium, lanthanum, praseodymium, neodymium, promethium, samarium, europium, lutetium, gadolinium, terbium, dysprosium, holmium, erbium, thulium and ytterbium, based on the weight of said zeolite.



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(54) Catalytic cracking process.

(57) Catalytic cracking processes wherein the cracking catalysts are prepared by: (1) contacting a mixture of a large pore zeolite and an inorganic oxide matrix at effective conditions of temperature, pH and time with a fluoro salt; and (2) ammonium exchanging the product of step (1) to provide a catalyst having less than 0.3 percent by weight Na₂O, based on total catalyst weight, or less than 2.0 percent by weight of the zeolite employed in the catalyst. Optionally, the zeolite used is provided with an effective amount of at least one cation selected from the class consisting of cerium, lanthanum, praseodymium, neodymium, promethium, samarium, europium, lutetium, gadolinium, terbium, dysprosium, holmium, erbium, thulium and ytterbium.

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EUROPEAN SEARCH REPORT

Application Number

EP 88 12 0757

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
D, X	US-A-4 588 701 (CHIANG et al.) * Claims 1-73; abstract; column 12, lines 4-34 * ---	1-6, 10-49	C 10 G 11/05
D, X	US-A-4 591 576 (CHIANG et al.) * Claims 1-74; abstract; column 12, lines 20-50 * -----	1-4, 7-47, 50-52	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 10 G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23-08-1989	Examiner MICHIELS P.
CATEGORY OF CITED DOCUMENTS			
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